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Synthesis, Spectroscopy and Magnetic Characterization of Five Dinuclear Copper(II) Complexes with 2, 3 or 4-Pyridinemethanol as the Ligand

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Abstract

The synthesis, spectroscopy and magnetic characterization of five new dinuclear copper(II) complexes are described. All five compounds have the general formula $[Cu_2(L)_4(O\text{-}R)_2](Cl)_2$ or $[Cu_2(L)_2(Cl)_2](Cl)_2$, in which R = CH_3 or H, L=2, 3 or 4-pyridinemethanol as L_2, L_3 or L_4, respectively. The title compounds consist of dinuclear units with bridging methoxo groups in $[Cu_2(L_4)_4(O\text{-}CH_3)_2](Cl)_2$, hydroxo groups in $[Cu_2(L_4)_4(OH)_2](Cl)_2$, and bridging chloro moeities in $[Cu_2(L_4)_4(Cl)_2](Cl)_2$, $[Cu_2(L_3)_4(Cl)_2](Cl)_2$ and $[Cu_2(L_2)_4(Cl)_2](Cl)_2$. Each dinuclear unit consisting of two ligands linked to each copper via the pyridine N atom, providing a $Cu_2N_2A_2$ unit (where A = OH, O-CH_3 or Cl). All complexes have been synthesized in a one-step reaction and characterized by elemental analysis, Fourier transform infrared (FTIR), electron spin resonance (ESR), and electronic spectra and by room temperature magnetic moments. The compounds exhibit antiferromagnetic interaction at room temperature. The UV-Vis spectra show three absorptions attributed to the d-d transition of the copper (II) ion, ligand→metal charge transfer and $\pi\rightarrow\pi^*$ or $n\rightarrow\pi^*$ transitions of the ligand. The FTIR spectra indicate a $Cu_2N_2A_2$ ring vibrating from 395 to 530 cm^{-1}. All complexes show a room temperature magnetic moment between 1.55 and 1.67 B.M. per copper atom. The X-band electron spin resonance (ESR) spectra of samples in DMF or DMSO frozen at liquid nitrogen temperature show a typical $\Delta m = 1$ transition.

Keywords: Dinuclear; Copper (II) complexes; Spin-spin coupling

Introduction

The structural and magnetic properties of many dinuclear compounds containing Cu_2O_2 systems have been investigated previously [1-4]. It is now generally accepted that the spin coupling in these compounds occurs through the bridging groups through a pathway that involves square-planar oxygen-bridged complexes

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of the type $[Cu_2(L)_4(O\text{-}R)_2]^{+2}$, where L = monodentate ligand. It is found that the isotropic exchange parameter, *2J*, is linearly related to the Cu-O-Cu angle, *Φ*, [5, 6]. This correlation has been explained in terms of molecular orbital theory [7]. It should be noted, however, that while *Φ* is very important, it is not the only structural parameter which can affect the value of *2J*. Sinn and co-workers have demonstrated that the distortion from planar toward tetrahedral environment at the metal center also markedly affects the magnitude of *2J*, although this distortion may not change the sign of *2J* [8-10]. Another factor contributing to the magnitude of *2J* is the effect of changing the electron density at the bridging atom [11]. The systematic study of small coordination compounds has already provided a more detailed understanding of the magnetic exchange phenomenon. In particular, dinuclear copper(II) complexes have been found to be very useful, considering the relatively simple single ion properties of the copper(II) ion that facilitates the interpretation of the magnetic data. The simplest bridging systems used are monoatomic bridges, such as hydroxo [12-14], alkoxo [15,16], chloro [17-20], bromo [21-24], fluoro [25,26], azido [27,28] and thiolato [29,30]. The most extensively studied series of compounds are represented by the planar dihydroxo-bridged dinuclear copper(II) complexes. These investigations have resulted in important insights in the superexchange mechanism taking place via double monoatomic bridges. Despite a vast number of experimental and theoretical studies, our understanding of the magnitude of the copper(II)-copper(II) coupling is still imperfect. We have been interested in how the effects of changing the ligand and R group on the bridging oxygen will change the magnetic properties of dicopper(II) complexes. In the present study, five dinuclear copper(II) complexes are reported with 2, 3 or 4-pyridinemethanol ligands of the general formula $[Cu_2(L)_4(Cl)_2]^{+2}$ or $[Cu_2(L)_4(O\text{-}R)_2]^{+2}$, where L is 2, 3 or 4-pyridinemethanol (Figs. 1A, 1B and 1C), and R is either a hydrogen or methyl group.

Materials and Methods

Experimental

Chemicals

All chemicals were of reagent grade purchased from Merck Chemical Company and used as received without further purifications.

Preparation of the Complexes

The coordination compounds were prepared according to the following general procedure:

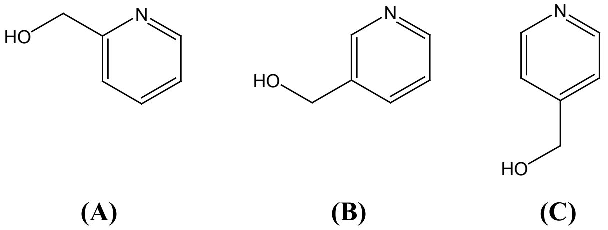
Complex $[Cu_2(4\text{-pyridinemethanol})_4(O\text{-}CH_3)_2]Cl_2$; ($C_1$)

One mmol of copper(II) chloride dihydrate and 2.1 mmol of 4-pyridinemethanol (scheme 1C) each dissolved in 25 ml of CH_3OH. The Cu(II) salt solution was then added slowly to the ligand solution, preventing any precipitation, filtered to remove any solids. After the solution stood for two days, the product was separated. Yield about 85%.

Elemental analysis for $Cu_2C_{26}H_{34}N_4Cl_2O_6$; (**$C_1$**); Found: C, 45.45; H, 4.41; N, 8.66; Cu, 18.65%. Cal.; C, 44.83; H, 4.92; N, 8.04; Cu, 18.24%.

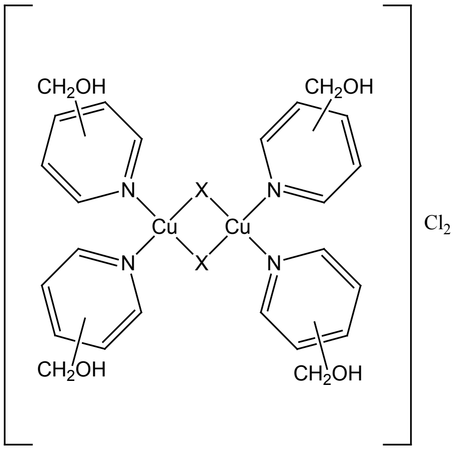
Complex $[Cu_2(4\text{-pyridinemethanol})_4(O\text{-}H)_2]Cl_2$; ($C_2$)

One mmol of copper (II) chloride dihydrate and 2.1 mmol of 4-pyridinemethanol each dissolved in 25 ml of C_2H_5OH. The Cu(II) salt solution was then added slowly to the ligand solution, preventing any precipitation, filtered to remove any solids. After the



(A) **(B)** **(C)**

Figure 1. Structure of Ligands.



X= Cl, OCH_3 or OH

Figure 2. Structure of Complexes.

Table 1. Spectroscopic data for all five complexes

Complex	UV-Vis (nm)	$G=(g_{II}-2)/(g_{\perp}-2)$	IR (Cu-O) IR (Cu-N) IR (Cu-Cl) (cm^{-1})	ESR Powder	ESR Solution in DMSO or DMF	μ_{Cu}(R.T.) B.M.
(C_1)	681, 293 262	4.6	486, 419, 397	g = 2.15	g_{II}=2.32 $A_{II} \approx 161\times10^{-4}$ $A_{N\perp} \approx 14\times10^{-4}$	1.55
(C_2)	710, 289 262	4.3	485, 460, 418	……	g_{II}=2.28 $A_{II} \approx 193\times10^{-4}$ $A_{N\perp} \approx 16\times10^{-4}$	1.57
(C_3)	888, 288 262	4.48	488, 435	g = 2.23	g_{II}=2.31 $A_{II} \approx 169\times10^{-4}$ $A_{N\perp} \approx 16\times10^{-4}$	1.62
(C_4)	880, 288 262	4.48	528, 424, 399	g = 2.23	g_{II}=2.30 $A_{II} \approx 175\times10^{-4}$ $A_{N\perp} \approx 17\times10^{-4}$	1.64
(C_5)	880, 293 262	4.4	478, 424, 397	g = 2.23	g_{II}=2.34 $A_{II} \approx 166\times10^{-4}$ $A_{N\perp} \approx 15\times10^{-4}$	1.67

solution stood for two days, the product was separated. Yield about 79%.

Elemental analysis for $Cu_2C_{24}H_{30}N_4Cl_2O_6$; (**$C_2$**); Found: C, 45.08; H, 4.44; N, 8.40; Cu, 18.73%. Cal.; C, 43.12; H, 4.52; N, 8.38; Cu, 19.01%.

Complex [Cu_2(4-pyridinemethanol)$_4$(Cl)$_2$]Cl_2; (C_3)

One mmol of copper(II) chloride dihydrate and 2.1 mmol of 4-pyridinemethanol each dissolved in 25 ml of CH_3CN. The Cu(II) salt solution was then added slowly to the ligand solution, preventing any precipitation, filtered to remove any solids. After the solution stood for two days, the product was separated. Yield about 87%.

Elemental analysis for $Cu_2C_{24}H_{28}N_4Cl_4O_4$; (**$C_3$**); Found: C, 40.58; H, 3.71; N, 7.76; Cu, 17.53%. Cal.; C, 40.86; H, 4.00; N, 7.94; Cu, 18.02%.

Complex [Cu_2(3-pyridinemethanol)$_4$(Cl)$_2$]Cl_2; (C_4)

This complex was obtained by a similar method as described for compound (**C_3**). Yield about 65%.

Elemental analysis for $Cu_2C_{24}H_{28}N_4Cl_4O_4$; (**$C_4$**); Found: C, 41.18; H, 3.18; N, 8.67; Cu, 18.20%. Cal.; C, 40.86; H, 4.00; N, 7.94; Cu, 18.02%.

Complex [Cu_2(2-pyridinemethanol)$_4$(Cl)$_2$]Cl_2; (C_5)

This complex was obtained by a similar method as described for compound (**C_3**). Yield about 70%.

Elemental analysis for $Cu_2C_{24}H_{28}N_4Cl_4O_4$; (**$C_5$**); Found: C, 39.35; H, 4.67; N, 7.45; Cu, 19.17%. Cal.; C, 40.86; H, 4.00; N, 7.94; Cu, 18.02%.

Physical Measurements

C, H and N determinations were undertaken using an Elementar Analysis System Gmb H Vario EL II. Cu determination was carried out on a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer operating at the wavelength of 324.7 nm. Electronic spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, and MgO was used as a reference. FTIR spectra were obtained in the 4000-390 cm^{-1} range as KBr disks using a Galaxy series FTIR 5000 spectrophotometer. The spectra were calibrated using polystyrene bands at 3028, 1601 and 1208 cm^{-1}. X-band electron paramagnetic resonance spectra were recorded on powder and frozen solutions of the complexes at both room and at liquid nitrogen temperatures in DMF or DMSO on an IBM electron spin resonance spectrometer using DPPH (g = 2.0036) as a standard. The room temperature magnetic moment of each complex was measured according to the Evans method. H NMR determination was carried out on a Bruker 300 MHz spectrometer.

Results and Discussion

Electronic Spectra

The spectroscopic data for all compounds (Fig. 2) are presented in Table 1. The electronic spectra of all complexes were obtained from a solid sample using diffuse reflectance technique and are very similar, illustrating similar geometries. The compounds show a broad band at 681 nm for complex $\mathbf{C_1}$, 710 nm for complex $\mathbf{C_2}$, 888 nm for complex $\mathbf{C_3}$, 880 for complex $\mathbf{C_4}$ and 880 nm for complex $\mathbf{C_5}$. These bands represent the ligand field transition for the CuN_2A_2 (A = OH, O-CH_3 or Cl) chromophore [30, 31]. The second absorption bands at 293, 289, 288, 288 and 293 nm for compounds $\mathbf{C_1}$, $\mathbf{C_2}$, $\mathbf{C_3}$, $\mathbf{C_4}$ and $\mathbf{C_5}$, respectively, are assigned to charge transfer from the non-bonding orbital of bridging atoms to the vacant copper(II) d orbitals [30, 32]. The last absorption band observed at about 262 nm for each of the complexes is associated with $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the ligand [33].

Infrared Spectra

The FTIR spectra were studied in detail, given the symmetry of the molecule. For the $Cu_2A_2L_4$ kind of compounds with D_{2h} symmetry, two important modes, B_{2u} and B_{3u}, associated with the vibration of the Cu_2A_2 unit were expected. This would potentially be of great help for the purpose of verifying the dinuclear structure for this type of compound [34-37]. The frequency of these modes is affected by the Cu_2A_2 planarity and the angle of the Cu-A-Cu units [38-40]. The IR spectra of the free ligands and the complexes were obtained in the range of 4000-400 cm^{-1}. All the bands present in the IR spectra of the free ligands were also observed in the spectra of the complexes. In the FTIR spectra a broad band observed at about 3500 cm^{-1} for all complexes which are ascribed to the OH vibrations of the ligand. The Cu-O vibrations of $\mathbf{C_1}$ and $\mathbf{C_2}$ are observed at (486 cm^{-1} and 419 cm^{-1}) and (485 Cm^{-1} and 460 cm^{-1}), respectively [41]. The Cu-N vibrations for $\mathbf{C_1}$, $\mathbf{C_2}$, $\mathbf{C_3}$, $\mathbf{C_4}$ and $\mathbf{C_5}$ are observed at 412 cm^{-1}, 418 cm^{-1}, 488 cm^{-1}, 527 cm^{-1} and 478 cm^{-1}, respectively. The remaining bands in this region belong to the Cu-Cl vibrations [42-45].

Magnetic Properties

The magnetic moment of all five complexes were determined by the Evans method [46,47]. This method is based on the principle that the position of a given proton resonance (t-butyl alcohol) in the spectrum of a molecule is dependent on the bulk susceptibility of the medium in which the molecule is found (Fig. 3). The shift of a proton resonance line of an inert substance due to the presence of paramagnetic ions is given by theoretical expression (1):

$$\Delta\upsilon/\upsilon_o = (2\pi/3)(\chi_\upsilon - \chi_{\upsilon'}) \qquad (1)$$

In this equation $\Delta\upsilon$ is the shift of υ_o (frequency) in the applied field, χ_υ is the volume susceptibility of the solution containing paramagnetic ions and $\chi_{\upsilon'}$ is the volume susceptibility of the reference solution. The values of 1.55, 1.57, 1.62, 1.64 and 1.67 B.M. per Cu(II) ion were found for complexes $\mathbf{C_1}$, $\mathbf{C_2}$, $\mathbf{C_3}$, $\mathbf{C_4}$ and $\mathbf{C_5}$, respectively. These are diminished μ_{eff} values relative to that for a typical d^9 Cu(II) complex ($\mu_B \geq 1.73$, but usually > 2).

Complex $\mathbf{C_1}$ has the lowest magnetic moment between the five complexes. This means there is a strong spin-spin interaction between the two copper(II) ions and it is predictable because an electron donor methyl group is attached to the bridging oxygen. The magnetic moment of complexes with chloride ion bridges are high, because the bulky chloride ions separate the two copper(II) ions far away from each other and the result is a weak spin-spin interaction.

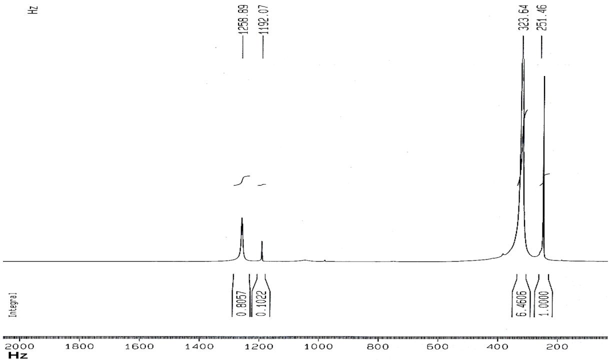


Figure 3. ^1H NMR spectra of complex C_1.

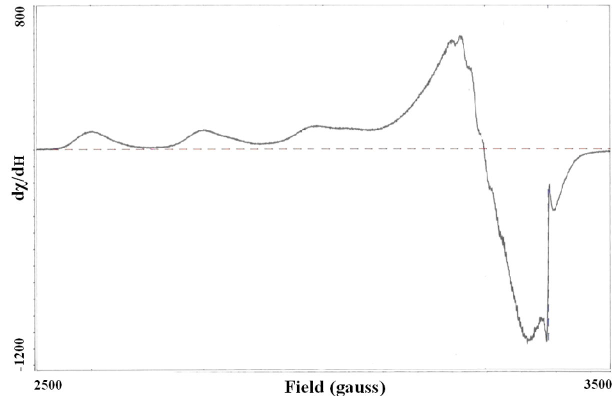


Figure 4. ESR spectra of complex C_1 in DMF at liquid nitrogen temperature.

The electron spin resonance (ESR) spectra of all five complexes in powder and in frozen solution form were recorded at X-band frequencies at room temperature and at liquid nitrogen temperature to aid in determining the ground-state configuration of copper(II) ions. In the solid state, the spectra were similar, with only a weak and broad signal ($g_{ave.}$ = 2.15, 2.23, 2.23 and 2.23 for **C_1, C_3, C_4** and **C_5**, respectively).

Such behavior is also found in the literature [48]. The observed frozen solution (77 K) ESR spectra of all compounds in DMSO or DMF show two bands located at $g_{||}$ = 2.32 and $g_{\perp}$ = 2.07 for **C_1**, $g_{||}$ = 2.31 and $g_{\perp}$ = 2.07 for **C_2**, $g_{||}$ = 2.31 and $g_{\perp}$ = 2.07 for **C_3**, $g_{||}$ = 2.30 and $g_{\perp}$ = 2.06 for **C_4** and $g_{||}$ = 2.34 and $g_{\perp}$ = 2.07 for **C_5** corresponding to the $\Delta M_S = \pm 1$ transition. These typical features for copper(II) complexes (Fig. 4) with $g_{||} > g_{\perp} > 2.0023$ and a large parallel hyperfine splitting, associated with the $d_{x^2-y^2}$ ground state in square-pyramidal geometry [49]. In the spectrum of each complex, the parallel region is clearly resolved and all four transitions derived from the Cu (I = 3/2) hyperfine splitting can be directly observed. These hyperfine lines for complexes **C_1**, **C_2**, **C_3**, **C_4** and **C_5** split the $g_{||}$ signal with an average spacing of 161×10^{-4} cm^{-1}, 193×10^{-4} cm^{-1}, 171×10^{-4} cm^{-1}, 175×10^{-4} cm^{-1}and 164×10^{-4} cm^{-1}, respectively. While in the perpendicular region of all complexes, the spectrum is not well resolved, some superhyperfine structure is observed. The lack of clear resolution in this spectral region is presumably due to the large number of overlapping $\Delta M_I = 0$ and $\Delta M_I > 0$ transitions and to the large intrinsic widths of the individual transitions. The structure observed in the perpendicular region of the spectra is due to nitrogen superhyperfine splitting of the ligands. The $A_{N\perp}$ value of $\approx 14\times10^{-4}$ cm^{-1} and the presence of six weak resolved peaks for the nitrogen superhyperfine structure of each complex, are in accordance with expectations for two N donors per copper(II) ions [50].

Acknowledgments

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